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13. ABSTRACT (Maximum 200 words)

The researchers formulated a theory to describe and calculate the dynamical dielectric response of classical interacting molecular liquids in terms of their corresponding static response functions. There are two basic ideas in this approach. One idea is to use a local effective field to take into account the long range "coherent" effects of the molecular interactions. These local fields are derived from the static structural properties of the liquid. The other idea to calculate the self-part of the van Hove correlation function from the solution of a Boltzmann transport equation in phase space in a number conserving relaxation time approximation. This smoothly interpolates between the hydrodynamic and free particle regimes. Thus they have obtained an important generalization of previous theories of molecular liquids, which only treated the self-part of the van Hove correlation function in the hydrodynamic limit, that is w=0 and q=0.

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Microscopic theory of the dielectric response of  
highly dispersive biological media

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and

Brian DeFacio, co-PI  
Professor

During the first year we formulated a theory to describe and calculate the *dynamical* dielectric response of classical interacting molecular liquids in terms of their corresponding *static* response functions. There are two basic ideas in this approach. One idea is to use a local effective field to take into account the long range "coherent" effects of the molecular interactions. These local fields are derived from the static structural properties of the liquid. The other idea to calculate the self-part of the van Hove correlation function from the solution of a Boltzmann transport equation in phase space in a number conserving relaxation time approximation. This smoothly interpolates between the hydrodynamic and free particle regimes. *Thus, we have obtained an important generalization of previous theories of molecular liquids, which only treated the self-part of the van-Hove correlation function in the hydrodynamic limit, that is  $\omega \approx 0$  and  $q \approx 0$ .*

The first year of this project was devoted to the calculation of the dielectric response of a "water-like" fluid. The "water-like" molecules are symmetric rigid rotors i.e. they have moments of inertia  $I_1 = I_2 \neq I_3$ , and no internal degrees of freedom. They carry rigid electric dipole moments. They interact with each other by dipole-dipole interactions at long range, and by a Lennard-Jones hard-core potential at short range. The first generation calculations were published with our Ph.D. candidate, now Dr. S.-H. Kim in Phys. Rev. A **46**, 7548-7560 (1992) and showed that this theoretical approach has considerable promise. It predicted two novel effects:

- (1) The existence of a peak in the real refractive index of the fluid at a frequency near to the characteristic frequency of precession of torque-free molecules, and (2) The possibility of a collective excitation of oscillating dipole moments - called the *dipolaron*. The first prediction finds support in the experimental data of Simpson et al. (J. Opt. Soc. Am. **69**, 1723 (1979)) for the infrared dielectric response of liquid water. The second is supported by molecular dynamics calculations by Pollock and Alder (Phys. Rev. Lett. **46**, 950 (1981)), but this effect is not yet

experimentally verified. However, we also found that the "water-like" fluid model is too simple to provide a quantitative description of the measured index of refraction of water in the far infrared frequency band although it works fairly well up to microwave frequencies and in the visible range. In particular, the inclusion of infrared vibrational degrees of freedom is essential to a quantitative agreement with experiments.

During the remainder of this project, the waterlike model was extended to higher frequencies by adding small amplitude oscillations of the molecule. Since water is a light molecule, this required the use of the Jacobi coordinates for the atoms together with group theory. The spring constants were chosen from the equilibrium point of a binding potential from the literature (using Jacobi coordinates). The complex dielectric response  $\epsilon_T(\omega, \vec{0})$  and index of refraction  $n(\omega)$  were calculated for the generalized model with these vibrations. Now this model is in good agreement with the experimental refractive index from DC to  $8 \times 10^{12}$  Hz and for all frequencies above  $10^{14}$  Hz. This result was published by Dr. Kim and the PI's in Phys. Rev. E **48**, 3172-3175 (1993).

Since the first two models were unable to describe the index of refraction in the far-infrared band, it is unclear whether the problem is the improper rotational inertia matrix of the waterlike model, the absence of quantum effects or even if the experiments in this region are wrong. The difficulty could also be a combination of two or all of these possibilities.

To investigate these questions, we next solved the generalization of our model to one with an asymmetric rotor whose values are given by those of a free water molecule. There were two complications involved in this generalization; the nonlinearity required that the Jacobi elliptic functions replace the trigonometric functions and with the correct inertia  $I_1 < I_2 < I_3$ , the electric dipole moment  $\vec{\mu}$  points in the 2 direction which is an *unstable* axis of rotation. For these reasons, it has not yet been possible to calculate the wave-vector  $\vec{q}$  dependence. The frequency dependences of the real and imaginary parts of the dielectric response and index of refraction were calculated and were found to *improve* the infrared behavior. However, this did not solve all of the problems nor provide an accurate agreement with experiment. The "free rotation" peak was reduced in size and new peaks were found in both the real and imaginary parts. The lack of wave-number information made it difficult to determine that the dipolaron collective mode remains in this improved model but a dip was observed in the  $q = 0$  response near the frequency where dipolaron was found before. We have written a manuscript entitled, *The dynamic dielectric response function of liquid water*, describing in detail these new findings, and submitted it for publication.

In addition, Dr. Kim and Brian DeFacio applied a generalization of the waterlike model to solutions of Hemoglobin in water for which the real and imaginary parts of  $\epsilon(\omega)$  have been measured. The model showed a surprising agreement with experiment, in fact, better than it did for pure liquid water. As soon as we understand this, the paper will be submitted for publication.

1. There were no patents nor inventions during this project.

## **2. Publications**

- a. S.-H. Kim, G. Vignale and B. DeFacio, Frequency and wave-vector dependent dielectric function of water-like fluid, Phys. Rev. A. **46**, 7548-7560 (1992).
- b. S.-H. Kim, B. DeFacio and G. Vignale, Refractive index of waterlike fluids, Phys. Rev. E. **48**, 3172-3175 (1993).
- c. S.-H. Kim, The Dynamic Dielectric Response of Liquid Water, Missouri University Physics Department, Dissertation co-advisors, G. Vignale and B. DeFacio, (August, 1993).
- d. B. DeFacio, S.-H. Kim and A. VanNevel, "Application of Squeezed States =Bogoliubov transformations to the statistical mechanics of water and its bubbles," *International Workshop on Squeezed States and Uncertainty Relations*, in *NASA Conf. Proc. XXXX*, Edited by D. Han, M. Rubin, Y. Shih and M.A. Man'kov (NASA, Greenbelt, in press) 13 pp.
- e. S.-H. Kim, G. Vignale and B. DeFacio, The Dynamic Dielectric Response of Liquid Water, (submitted).

## **3. Students Supported**

S.-H. Kim: April 1991 – Oct. 1993, Research Assistant, now a Post-doc in the Physics Department at the University of Minnesota.  
D.M. Patterson: Summer 1992, Research Assistant, Microsoft Corporation, 1992-4, presently on the Scientific Staff at Martin Marietta, Philadelphia, PA.

## **4. Papers Presented**

- a. American Physical Society, 1992 March Meeting, Indianapolis, S.-H. Kim, et al., Statistical Mechanics Section, B. DeFacio, et al., Biophysics Section.
- b. Midwest Solid State Theory Meetings: Kim, et al., F'92, Iowa State University, Ames, IA, Kim, et al., F'93, University of Wisconsin, Madison
- c. American Physical Society, 1993 March Meeting, Seattle; Kim, et al., Statistical Mechanics Section.
- d. University of Cincinnati, *Theory Seminar on Water*, Department *Colloquium on Wavelets*, B. DeFacio.
- e. AFOSR Workshop on Electromagnetism, San Antonio, TX, Jan. 4-7, 1994; G. Vignale on the

fundamental many-body theory of this project; B. DeFacio on some of the calculations using our models.

## 5 . Other

B. DeFacio was elected to Fellowship of the American Physical Society in Nov., 1993. A copy of the citation is enclosed.

In summary, a new model has been formulated for the dielectric properties of liquid water and has both added to the understanding of this important problem, and contributed to the education of graduate students.

Respectfully submitted,

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Associate Professor

*Bruce de Facio*  
B. DeFacio  
Professor